Adsorption isotherm and kinetic modelings of Pb(II) and Cu(II) uptake by *Dimocarpus longan* peels

Meilia Innes Kurniawan, Edison Munaf and Rahmiana Zein*

Laboratory of Environmental Analytical Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padang, Indonesia

_____

ABSTRACT

Dimocarpus longan peels, the low-cost adsorbent, was investigated of removing Pb(II) and Cu(II) ions from aqueous solutions. Batch adsorption studies were conducted to examine their optimum conditions. For adsorption of Pb(II), the optimum pH solution, contact time and stirring speed were 5.0, 90 min and 200 rpm, respectively. Those values for Cu(II) ions were 4.0, 90 min and 100 rpm, respectively. Based on the correlation of determination (R), several kinetic models were able to describe the equilibrium contact time data in the order : $2^{nd} > 1^{st} > Intraparticle > Elovich$. Data obtained from variation of initial concentrations were found to fit the Langmuir, Freundlich, D-R and Temkin adsorption isotherms with R of D-R ≈ Freundlich > Temkin > Langmuir. The maximum capacity for Cu(II) ions was 8.2175 mg/g. Meanwhile, Pb(II) ions fit the Linear adsorption isotherm, so that no maximum capacity to be found.

Keywords*: Adsorption isotherm, Kinetic modeling, Dimocarpus longan Peels, Toxic metals*

_____

INTRODUCTION

Metal ions were reported as priority pollutants, due to their mobility in natural water, ecosystems and their toxicity. The problem associated with metal ions pollution was that they were not biodegradable and were highly persistent in the environment. Thus they could be accumulated in living tissues, causing various diseases and disorders. Heavy metals toxicity could result in damage or reduced mental and central nervous function and damage to blood composition, lungs, kidneys, liver and other vital organs [1].

It was a necessity to remove metal ions from wastewater before it could be discharged. Many physicochemical methods had been developed for the removal of metal ions from aqueous solutions. However those methods had disadvantages such as secondary pollution, high cost, high energy input, large quantities of chemical reagents or poor treatment efficiency at low metal concentration.

Biosorption had emerged as an alternative and sustainable strategy for cleaning up water. Biosorption used inexpensive biomaterials to sequester environmental pollutants from aqueous solutions by a wide range of physicochemical mechanisms, including ion exchange, chelation, complexation, physical adsorption, and surface microprecipitation [1]. In this study, the biosorption of Pb(II) and Cu(II) by *Dimocarpus longan* peels from single and binary mixtures were investigated by batch adsorption.

To develop the adsorption mechanism, kinetic and isotherm analysis had been included. For this purpose we would determine the optimum biosorption conditions as a function of pH, contact time, stirring speed, initial metal ion concentration and amount of biosorbent dose in the biosorption of Pb(II) and Cu(II) by *Dimocarpus longan* peels.

_____

EXPERIMENTAL SECTION

In present works, the biosorption experiments were conducted by using stock standard solution (1000 mg/L) of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ in 0.5 M HNO_3. These solutions were purchased from Merck (Germany). Working standard solutions were prepared just before used by the appropriate dilution of the stock solutions.

Peels preparation and characterization: *Dimocarpus longan* fruits (Fig. 1a) were collected from flea market of Payakumbuh city. Then their peels (Fig. 1b) were air-dried in the room for one weeks and ground using crusher (Fritsch, Germany). After that the powder was ground again using mortal grinding (Fritsch, Germany). The working powder (Fig. 1c) was activated by soaking 20 g biomass in excess of 80 mL HNO_3 0.01M for 2 h, followed by washing thoroughly with deionized water and then air-dried. The resulting pale brown powder could be stored for a long time.

The dry powder was treated with 25 mL Pb(II) or Cu(II) 10 mg/L, shaked for 1.5 h with 100 rpm and then was filtered. To determine the total amount of Pb(II) or Cu(II) left in the solution, these pale yellow filtrated (pH about 6) were analyzed by AAS (VARIAN SPECTRAA240) at 217.0 and 324.8 nm, respectively. There were several parameters to be treated to get the optimal adsorption of heavy metal ions with biomass.

The amount of adsorbed metal ions per gram of the biomass (biosorption capacity, Q) was obtained using the following equation:

$$Q = \frac{(Co - Ce)V}{m}$$
(1)

Where Co and Ce were initial and equilibrium metal ions concentration in solutions (mg/L), respectively; V was volume of the solution (L); m was the amount of biomass (g).

RESULTS AND DISCUSSION

Effect of initial pH:
Figure 2 showed the maximum adsorption of Pb(II) on peels was 0.9691 mg/g at pH 5. The optimal uptake of Cu(II) for this biosorbents at pH 4 was 0.5529 mg/g. Thus, the affinity of cationic species towards the functional groups present in that biosorbents was strongly dependent on the pH. Metal ions undergo hydrolysis as the pH increases (pH > 5), so that several hydroxyl low soluble species could be formed, $Pb(OH)_2$ or $Cu(OH)_2$. Adsorption was also not appropriate when pH < 3 [2].

Castro *et al.*[3] investigated the biosorption of Pb(II) with banana peel also got the optimal pH for biosorption as 5. Nawaz *et al.*[4] reported that the maximum pH by red rose waste was 5 for Pb(II). Naidu *et al.*[5] who studied adsorption kinetic and thermodynamic of Pb(II) by *Tectona grandis* L.F found the optimum pH of Pb(II) was 5. Kurniawan *et al.*[6] used *Annona muricata* L. seeds for biosorption of Pb(II) and Cu(II) presented the maximum pH 3 and 4, respectively. Singh *et al.*[7] claimed that the optimum pH of Cu(II) was 4. Argun *et al.*[8] investigated about biosorption of heavy metal by modified oak sawdust found the optimum pH of Cu(II) was 4. Ngah *et al.*[9] reported the optimum pH of Cu(II) was 4.

Effect of Contact time:
The biosorption capacity of metal ions was evaluated as a function of contact time. The initial concentration of metals was 10 mg/L. The metal uptake was rapid for Pb(II) at the beginning of the process and gradually increased as time progressed to attain equilibrium after 90 min, then decreased. For Cu(II) the amount of metal uptake was increased slightly, till 90 min, and then decreased (Fig. 3). The metal uptake capacity of biomass at 10 mg/L metal solution was different for two metals. The highest metal uptake obtained for Pb(II) and Cu(II) on peels were 0.9691 and 0.5529 mg/g, respectively of dried biomass. This might be due to the ionic radii and favorable sites for biosorption of those two ions were different (was not shown).

Naidu *et al.*[5] used *Tectona grandis* L.F for biosorption of Pb(II) found the optimum contact time was 75 min. Moreover, Farhan *et al.*[10] used *Ficus carcia* leaves for biosorption of Pb(II), the maximum contact time was 80 min. Uluozlu *et al.*[11] reported that the optimum contact time of Pb(II) was 90 min. Yang *et al.*[12] who studied adsorption of Pb(II) from solution using peanut shell as biosorbent, the optimum contact time for Pb(II) was reached within 100 min. Singh *et al.*[7] used *Spirogyra* sp. for biosorption of Cu(II) obtained the optimum contact time for Cu(II) was 120 min. Sethu *et al.*[13] also represented the optimum contact time of Cu(II) was 120 min. Slaiman *et al.*[14] investigated biosorption of heavy metals ions by bamboo reported that the optimum contact time of Cu(II) was 120 min. Njoku *et al.*[15] showed that the optimum contact time for Cu(II) was 120 min.

_____

Adsorption Kinetics:
In order to test the experimental data of these works, kinetic models have to be used. The kinetics studied of Pb(II) and Cu(II) adsorption were carried out by analyzed those data that formerly were used to determine optimum condition of contact time. In order to distinguish the kinetics equation based on the concentration of a solution from the adsorption capacity of solids, this second-order or first-order rate equation has been called as a pseudo second-order or first-order ones.

For pseudo first-order rate, samples were taken at preset time intervals up to 75 min for Pb(II) and Cu(II), respectively. The pseudo first-order rate:

$$\frac{dQ}{dt} = k_1(Qe - Qt) \tag{2}$$

In this case the kinetic order was one with respect to the number of available sites for the exchange reaction. The linier first-order rate expression was generally expressed as:

$$-Ln\,(Qe - Qt) = k_1.t - Ln\,Qe \tag{3}$$

Where Qe and Qt were the amount of Pb(II) and Cu(II) ions adsorbed at equilibrium (mg/g) and at time t (min), k_1 was the pseudo first-order rate constant (min^{-1}).

For pseudo second-order rate, samples were taken until 120 min for Pb(II) and Cu(II), respectively. The pseudo second-order rate:

$$\frac{dQ}{dt} = k_2(Qe - Qt)^2 \tag{4}$$

It was assumed that the kinetic order was two with respect to the number of available sites for the exchange reaction. The linear form of pseudo second-order can be written:

$$\frac{t}{Qt} = \frac{1}{k_2.Qe^2} + \frac{t}{Qe} \tag{5}$$

where k_2 was the pseudo second-order rate constant (g mg^{-1} min^{-1}).

Usually, when the initial concentration of solute was low, then the adsorption process obeys the pseudo second-order model. Conversely pseudo first-order models could be applied to higher initial concentrations[16].

Elovich equation that was derived through the work of Zeldowitsch was generally expressed as:

$$\frac{dQt}{dt} = \alpha\exp(-\beta Qt) \tag{6}$$

α and β were constants during experiment. The constants α could be regarded as initial rate since $\frac{dQt}{dt} = \alpha$ as Qt = 0. Integration of equation 6 assuming the initial boundary condition Qt = 0 at t = 0 gives:

$$Qt = \frac{1}{\beta}\ln(1 + \alpha\beta t) \tag{7}$$

To simplify Elovich equation, Chien and Clayton assumed that $\alpha\beta t \gg 1$ and by applying the boundary conditions of $Q_t = 0$ at t = 0 and Qt = Qt at t = t, then equation (7) becomes:

$$Qt = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{8}$$

Where α was the initial adsorption rate (mg g^{-1} min^{-1}), and β was related to the extent of surface coverage and activation energy for chemisorption (g/mg). These constants could be obtained from the intercept and the slope of a straight line plot of ln t against Qt[17-20].

Going deeply into the biosorption mechanism, many researchers studied the application of the intraparticle diffusion model for their biosorption data. The overall rate of adsorption could be described by the following three steps: (1) film or surface diffusion where the sorbate is transported from the bulk solution to the external surface of sorbent,

(2) intraparticle or pore diffusion, where sorbate molecules move into the interior of sorbent particles, and (3) adsorption on the interior sites of the sorbent[1].

The intraparticle diffusion of Weber and Morris suggests proportionality between the adsoption capacity and the square root of the time. The model's equation was expressed by:

$$Qt = K_{(i)}t^{0.5} + C_{b(i)} \tag{9}$$

K (mg g^{-1} min$^{-0.5}$) was the intraparticle diffusion parameter, and C$_b$ (mg/g) was the thickness of the boundary layer at stage (i).

The shape of the plots of Qt against t$^{0.5}$ gave much information about the biosorption mechanism. These plots were either presented by "one single line" or "multiple lines". If the Weber–Morris plot of Qt versus t$^{0.5}$ gave a straight line, then the adsorption process was controlled by intraparticle diffusion only. The intercept of these plots reflects also the boundary layer effect. Larger the intercept, greater was the contribution of the surface sorption in the rate controlling step[1].

We started with low initial metal ions concentration. As could be seen from Fig. 4 and 5, the pseudo-second order kinetic models were more suitable than first-order for modeling the adsorption of Pb(II) and Cu(II) by *Dimocarpus longan* peels (R of first-order was less than that of second-order for both Pb(II) and Cu(II) ions). The rate constant (k$_1$) of Pb(II) and Cu(II) were 0.0403 and 0.0082 min^{-1} (Fig. 4). However, the rate constant (k$_2$) of Pb(II) and Cu(II) were 0.2277 and 0.1944 g min^{-1} mg^{-1} (Fig. 5). Thus. the rate constants of Pb(II) adsorption were greater than those of Cu(II). Both electronegativity and ionic radii of Pb(II) were greater than that of Cu(II). There might be a stronger chemical and affinity for Pb(II) than for Cu(II) on biosorbent.

Raju *et al.*[21] used *Carica papaya* leaf powder for biosorption of Pb(II) showed that pseudo-second order model was better compared to the pseudo-first order. Hadi *et al.*[22] investigated the removal of Cu(II) from water by adsorption on papaya seed, also found the kinetic data fit the pseudo-second order.

Fig. 6 illustrated that the correlation coefficient of Pb(II) was better than that of Cu(II) ions for Elovich equation, with β for Pb(II) and Cu(II) were 7.8064 and 19.1571 mg/g, respectively. This β value reflected the activation energy for chemisorption. Thus, Pb(II) would be adsorbed easier than Cu(II) by peels. This in agreement with k$_1$ and k$_2$ for Pb(II) were greater than those of Cu(II) from pseudo-first order and second. Adebayo *et al.*[20] who studied isotherm, kinetic and thermodynamic of Pb(II) by *Streblus asper* found β was 4.39 mg/g.

Fig. 7 indicated that both Pb(II) and Cu(II) on *Dimocarpus longan* peels followed a two step intraparticle diffusion process. The correlation coefficient of Pb(II) in the first and second stage were better than that of Cu(II) ions. The second step was always faster than of the first. Those were K$_1$ = 0.06275; K$_2$ = 0.1149 (mg g^{-1} min$^{-0.5}$) for Pb(II) and K$_1$ = 0.01248; K$_2$ = 0.02529 (mg g^{-1} min$^{-0.5}$) for Cu(II). Again intraparticle results were in agreement with pseudo order and Elovich equations, the rate of Pb(II) adsorption on peels was greater than that of Cu(II). Zheng *et al.*[23] investigated sorption isotherm and kinetic modeling of aniline on Cr-bentonite, found a two step intraparticle diffusion process. Gulipalli *et al.*[24] used rice husk ash for Se(IV) biosorption and also described a two step intraparticle diffusion process.

Effect of Stirring Speed:
Biosorption studies were carried out in a shaker at pH 5.0 and 4.0 for Pb(II) and Cu(II) on peels, respectively. The stiring speed was varied from 30 to 250 rpm. Figure 8, illustrated the influence of the stirring speed on the biosorption, showed that the optimum values were obtained at 200 rpm for Pb(II) and 100 rpm for Cu(II). Stirring are required since a thin liquid film surrounding the biomass particles offered resistance to the mass to adsorb the ion by diffusion. However, the higher stirring speed might cause complex between ion and biomass was ruptured.

Naidu *et al.*[5] used *Tectona grandis* L.F for biosorption of Pb(II) found the maximum stirring speed was 180 rpm. Stojanovic *et al.*[23] investigated biosorptive removal of Pb(II), Cd(II) and Zn(II) ions from water by *Lagenaria vulgaris* shell got the optimal of stirring speed for Pb(II) was 200 rpm. Kurniawan *et al.*[6] studied *Annona muricata* L. seeds for biosorption of Pb(II) and Cu(II), did find the optimum stirring speed were 150 and 100 rpm, respectively.

Effect of Initial Ion Concentration:
Figure 9 showed the heavy metal ion biosorption capacities of *Dimocarpus longan* peels as a function of the initial concentration of Pb(II) and Cu(II) ion within the aqueous solution. The amount of metal ions adsorbed per unit mass

of peels increased with an increased in initial metal ion concentrations for Pb(II) and Cu(II), and then decreased for Cu(II). This increased could be due to the increased in electrostatic interactions (related to covalent interactions).

Adsorption Isotherm:
An adsorption isotherm described the relationship between the amount of adsorbate uptaken by the adsorbent and the adsorbate concentration remaining in solution. This isotherm was derived from equilibrium constant of the interaction of adsorbate with adsorbent. In the present study, the equilibrium data for Pb(II) and Cu(II) adsorption on *Dimocarpus longan* peels were evaluated by the Langmuir, Freundlich, Linear, Dubinin-Radushkevich (D-R) and Temkin models.

The most commonly used isotherms for the application by adsorbents in wastewater treatment were the Freundlich and Langmuir isotherms. The Langmuir isotherm was based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, the energy of adsorption constant and there was no transmigration of adsorbate in the plane of the surface. The Langmuir model was described by the following equation[16]:

$$Qe = \frac{K_L.Qm.Ce}{1+K_L.Ce} \tag{10}$$

A linier expression for the Langmuir isotherm could be written as:

$$\frac{Ce}{Qe} = \frac{1}{Qm.K_L} + \frac{Ce}{Qm} \tag{11}$$

Where Qm was the maximum metal uptake corresponding to the saturation capacity (mg/g), K_L was energy of adsorption (L/mg), Qe was the amount of metal adsorbed on the biomass (mg/g) and Ce was equilibrium metal concentration in solution (mg/L). In contrast, the Freundlich isotherm could be used for non-ideal adsorption that involves heterogeneous. The general Freundlich equation was given as:

$$Qe = K_f.Ce^{1/n} \tag{12}$$

The linear form of this model was:
$$Ln\ Qe = Ln\ K_f + \left(\frac{1}{n}\right).Ln\ Ce \tag{13}$$

Where K_f was Freundlich constant (as a measure of the degree or strength of adsorption), $\frac{1}{n}$ was the heterogeneity factor and n indicated the sorption capacity and the sorption intensity of system. The value of n > 1 observed from Freundlich isotherm indicated that sorption was favorable, heterogeneous and chemisorption. When n = 1, Freundlich isotherm was claimed to linear adsorption isotherm. As the Freundlich isotherm equation was exponential, it could only be reasonable applied in the low to intermediate concentration ranges. Langmuir and Freundlich models could be applied at a constant pH[26,27].

Linear isotherm was the simplest used adsorption isotherm equation. Linear isotherm equation was conventionally expressed in terms of the distribution coefficient, K (in L/g):

$$Qe = K.Ce \tag{14}$$

The more general isotherm was D-R since it did not assume a homogenous surface or constant sorption potential. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions. The Isotherm of D-R was determined from following equation:

$$\ln Qe = Ln\ Q_D - B\varepsilon^2 \tag{15}$$

Where B was denoted as the isotherm constant ($mol^2\ J^{-2}$), Q_D was the theoritical saturation capacity (mg/g). Meanwhile, the parameter ε was the polanyi potential which was calculated as:

$$\varepsilon = RT\ ln\left(1 + \frac{1}{Ce}\right) \tag{16}$$

Where R was the gas constant (8.314 J $mol^{-1}K^{-1}$) and T was the absolute temperature (K).

The mean free energy E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity, in J/mol) could be computed by the relationship:

$$E = \frac{1}{(2B)^{1/2}}$$ (17)

A sorption process was generally considered as physical if E < 8 kJ/mol and as chemical when E value lies between 8 and 16 kJ/mol[27].

Temkin isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. Its derivation was characterized by a uniform distribution of binding energies (up to some maximum binding energy), which was expressed in the following equation:

$$Qe = \left(\frac{RT}{b_T}\right) Ln\, Ce + \left(\frac{RT}{b_T}\right) Ln\, K_T$$ (18)

Where K_T was the constant of Temkin isotherm (Lg^{-1}) and b_T was the Temkin isotherm constant related to the heat of adsorption (kJ mol^{-1})[28].

Fig. 10 described the linearized Langmuir isotherm adsorption of Cu(II) on peels. Based on the slope of Fig. 10, the theoretical values of Qm for Cu(II) ion was 9.3985 mg/g. However, that experimental value was 8.2175 mg/g (Fig. 9). The linearized Freundlich isotherm adsorption was shown in Fig. 11. The n value in Freundlich equation was found to be 1.4035, then adsorption were favorable, heterogeneous and chemisorption. Compared to the correlation coefficient of Fig. 10 and 11, Freundlich was better fit than Langmuir model for Cu(II). Kurniawan *et al.*[6] used *Annona muricata* L. seeds for biosorption of Pb(II) and Cu(II) did find the Freundlich model was more favorable than Langmuir. Gonzalez *et al.*[29] who studied biosorption of Pb(II) by *Agave tuquilana* W. biomass also indicated that the Freundlich fit better than Langmuir model. According to Awwad *et al.*[26] used olive leaves, the n value in Freundlich equation was 1.45. Wu *et al.*[30] used activated anaerobic sludge for biosorption Cu(II) showed that n value in Freundlich equation was 1.43.

Adsorption of Pb(II) ion on peels obeyed the linear adsorption isotherm (Fig. 12), with K was 0.4509 L/g. This plot did not pass the origin, indicated that more than one step adsorption process would occur. This models of adsorption of Pb(II) and Cu(II) on peels were not the same, since these ions were adsorbed at different sites (was not shown).

Figure 13 showed the linearized D-R isotherm for Cu(II) adsorption on peels. In these plot Q_E was in mol/g and Ce (mol/L). The values of E and Q_D computed from the slope and the intercept of that graph were 8279.5165 J/mol (8,2795 kJ/mol) and 5.9337×10^{-4} mol/g (37.68 mg/g), respectively. Thus, Elovich, Freundlich and D-R equations predicted that Cu(II) was chemically absorbed by peels. Prasad *et al.*[31] used potato peels for Fe(III) adsorption showed that E = 10.78 kJ/mol and $Q_D = 3.48 \times 10^{-3}$ mol/g. Hasany *et al.*[32] investigated the adsorption of Cd(II) on coconut husk found E = 8.5 kJ/mol and $Q_D = 3.51 \times 10^{-2}$ mol/g. Wu *et al.*[30], studied biosorption of Cu(II) on aerobic sludge informed that E = 8.01 kJ/mol and $Q_D = 7.2 \times 10^{-3}$ mol/g.

Figure 14 illustrated the linearized Temkin equation for Cu(II) on peels, with R = 0.8784. The calculated isotherm constant $K_T = 0.2607$ L/mg, and $b_T = 1.5716$ kJ/mol. This positive value of b_T characteristic of an endothermic interaction between sorbate and sorbent. Tichaona *et al.*[33] who studied biosorption of Cu(II) by *Vigna subterranea* found $K_T = 0.18$ L/mg, and $b_T = 0.30$ kJ/mol.

Effect of biomass dosage:
Fig. 15 showed the heavy metal ion biosorption capacities of *Dimocarpus longan* peels as a function of the biomass dosage of Pb(II) and Cu(II) ion within the aqueous solution. The biosorption capacity (Q) decreased as the dosage of biomass increased.
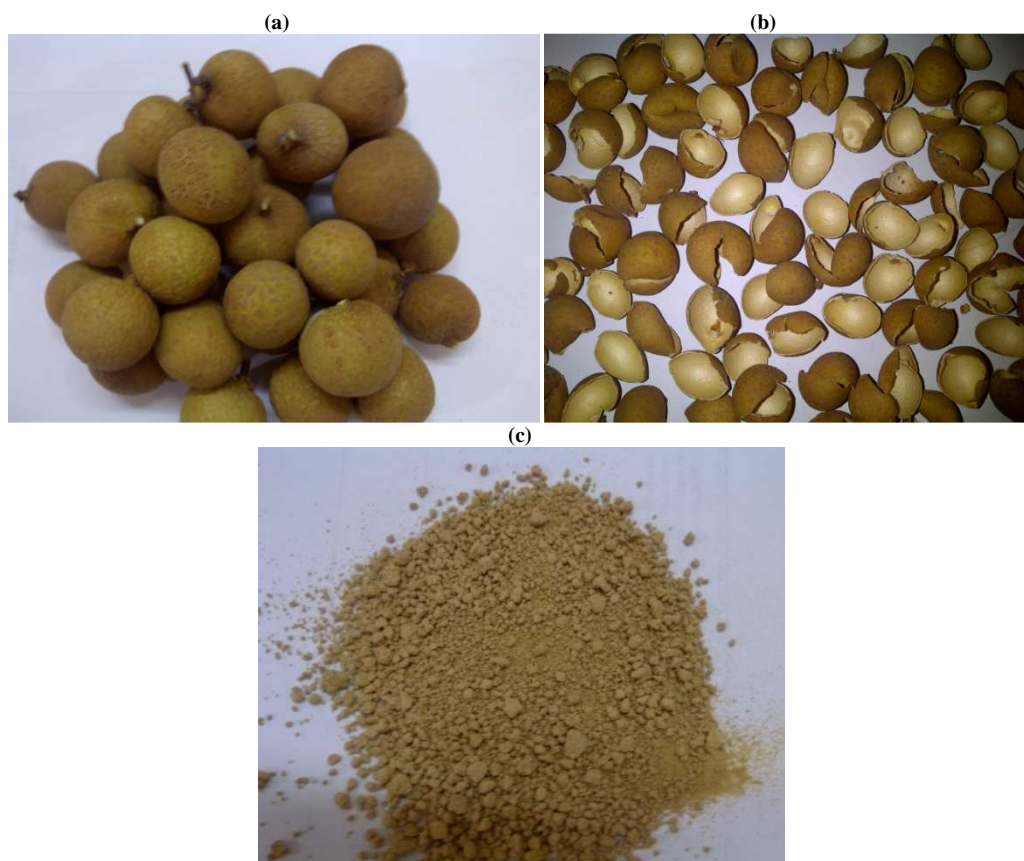
_____

(a) (b)

(c)

Figure 1.(a) *Dimocarpus longan* **(b)** *Dimocarpus longan* **peels (c) dry powder of** *Dimocarpus longan* **peels**
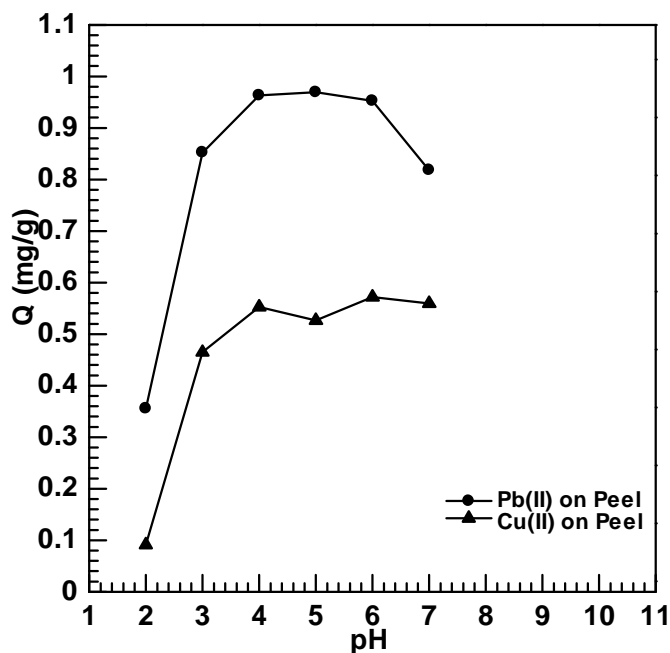

Figure 2. Effect of initial pH on Pb(II) and Cu(II) biosorption by *Dimocarpus longan* **peels; 25 mL metal solution, concentration = 10 mg/L; mass of biosorbent = 0.25 g; contact time = 90 min; stirring speed = 100 rpm; biosorbent size = 180 µm**
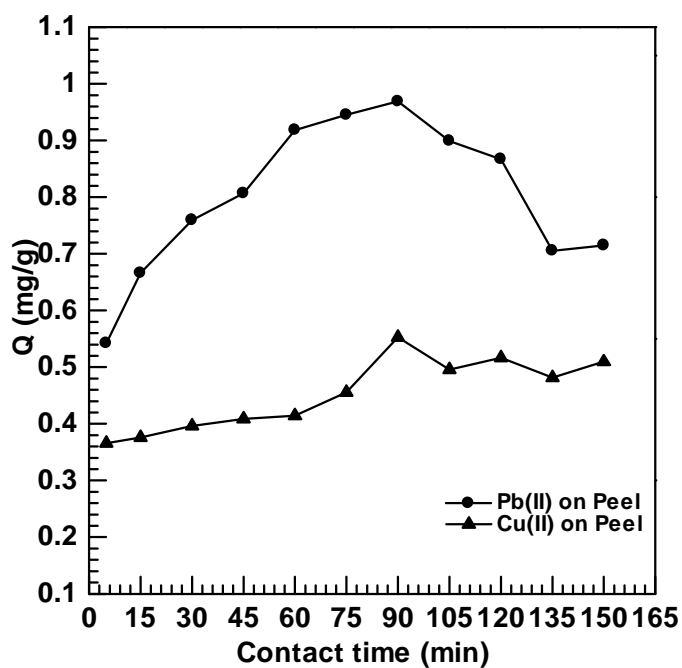
_____

Figure 3. Effect of contact time on Pb(II) and Cu(II) biosorption by *Dimocarpus longan* peels; 25 mL metal solution, concentration = 10 mg/L; pH of Pb(II) and Cu(II) on peels = 5.0 and 4.0; mass of biosorbent = 0.25 g; stirring speed = 100 rpm; biosorbent size = 180 μm
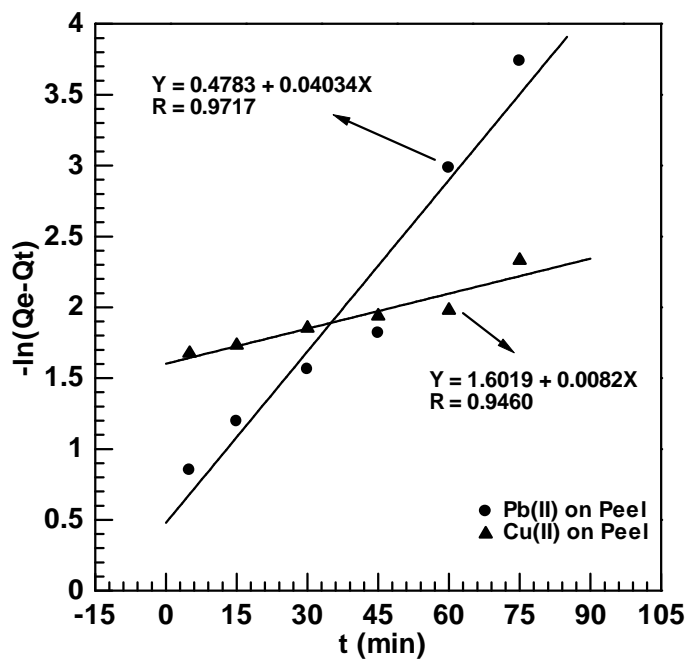
Figure 4. Pseudo-first order kinetic model for Pb(II) and Cu(II). Data were taken from Figure 3

_____
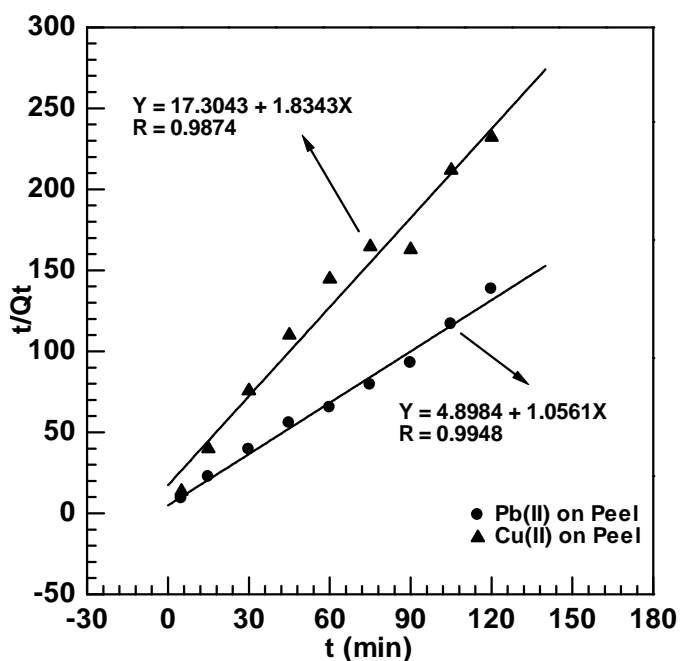
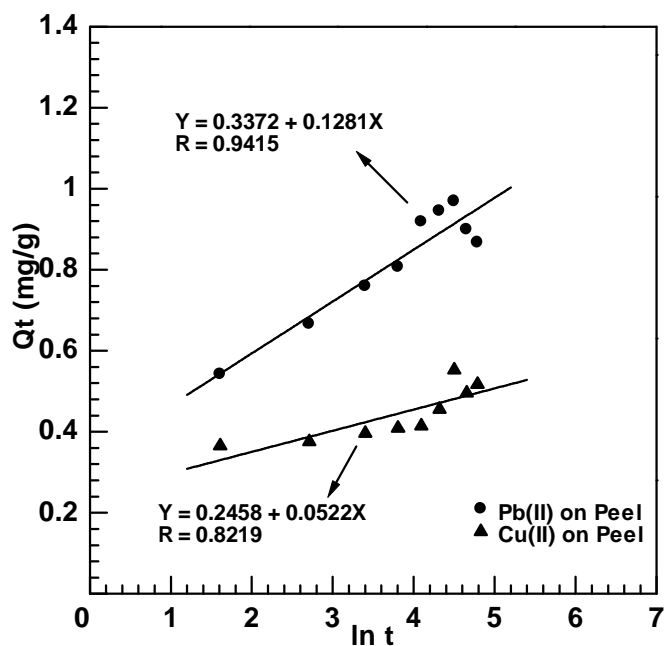**Figure 5. Pseudo-second order kinetic model for Pb(II) and Cu(II). Data were taken from Figure 3**

Figure 6. Elovich equation for Pb(II) and Cu(II). Data were taken from Figure 3

_____
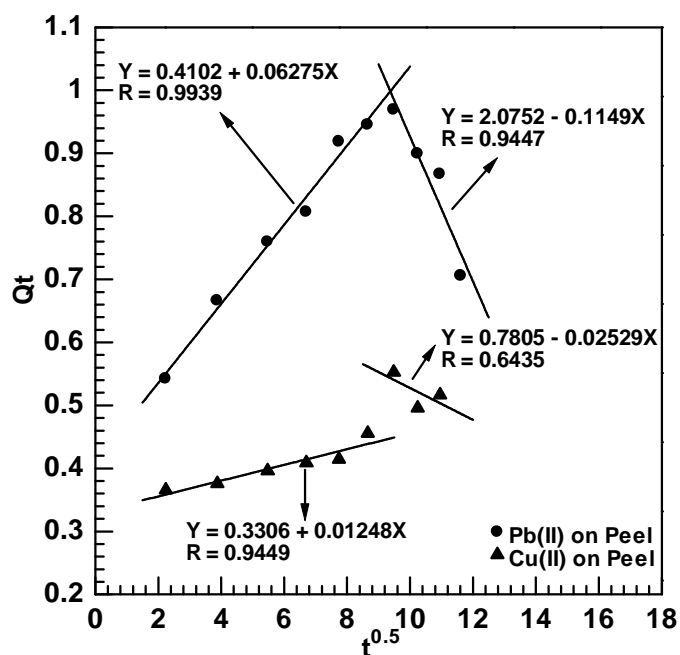
Figure 7. Intraparticle diffusion equation for Pb(II) and Cu(II). Data were taken from Figure 3
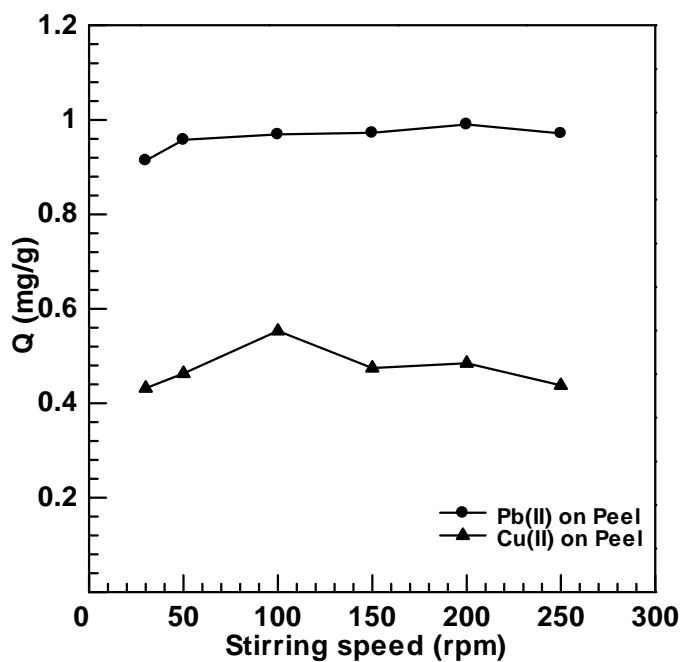

Figure 8. Effect of stirring speed on Pb(II) and Cu (II) biosorption by *Dimocarpus longan* peels; 25 mL metal solution, concentration = 10 mg/L; pH of Pb(II) and Cu(II) on peels = 5.0 and 4.0; mass of biosorbent = 0.25 g; contact time = 90 min for both ions; biosorbent size = 180 μm
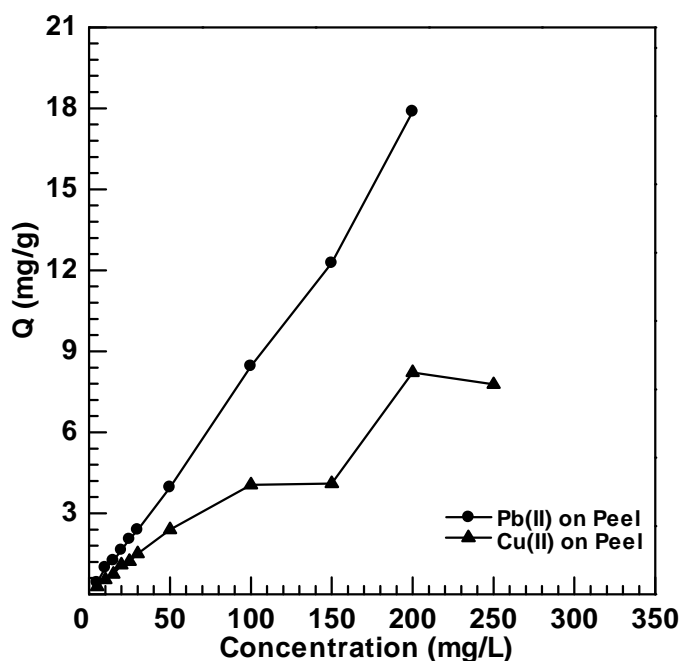
_____

Figure 9. Effect of initial metal ion concentration on Pb(II) and Cu(II) biosorption by *Dimocarpus longan* peels; 25 mL metal solution, concentration = 10 mg/L; pH of Pb(II) and Cu(II) on peels = 5.0 and 4.0; mass of biosorbent = 0.25 g; contact time = 90 min for both ions; stirring speed = 200 and 100 rpm for Pb(II) and Cu(II) on peels; biosorbent size = 180 μm
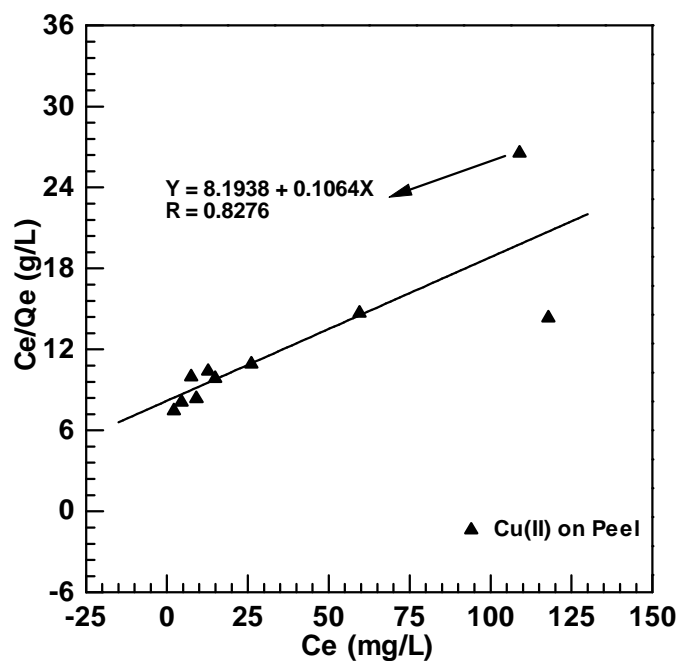

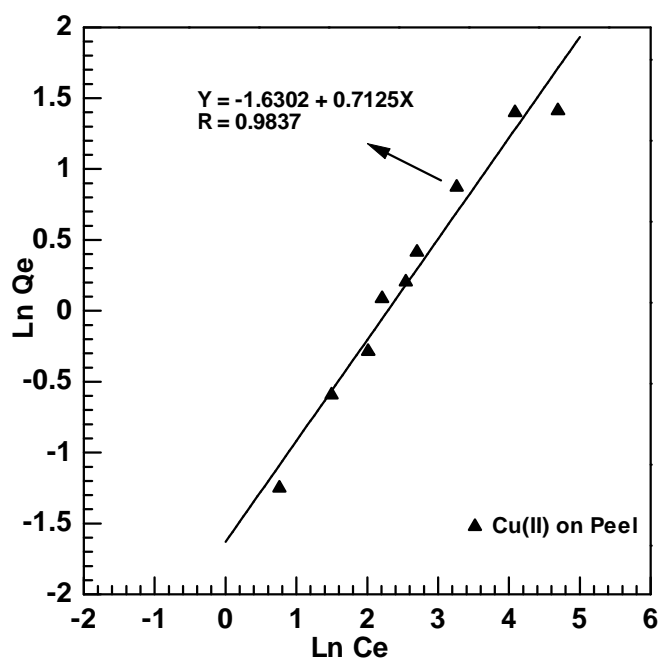
Fig. 10. Linearized Langmuir equation for Cu(II)

_____

Y = -1.6302 + 0.7125X
R = 0.9837

▲ Cu(II) on Peel

Ln Ce

Fig. 11. Linearized Freundlich equation for Cu(II)

Y = 0.1715 + 0.4509X
R = 0.9862

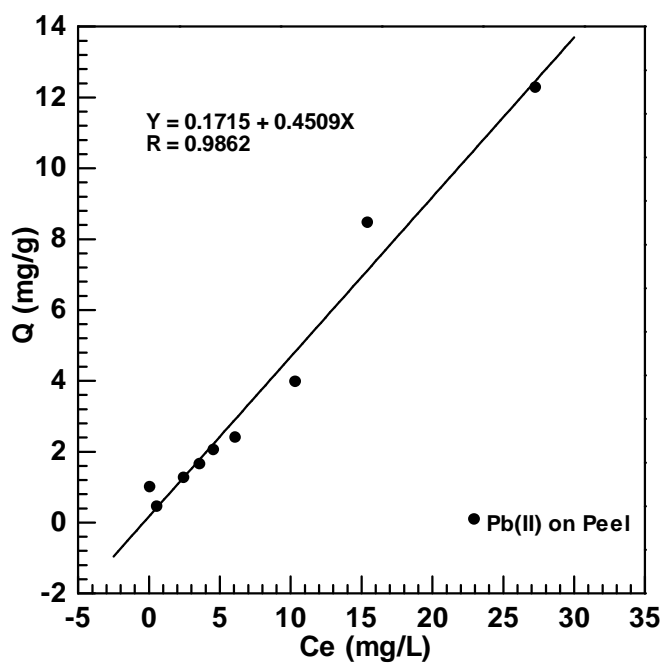● Pb(II) on Peel

Ce (mg/L)

Fig. 12. Linear adsorption isotherm equation for Pb(II)
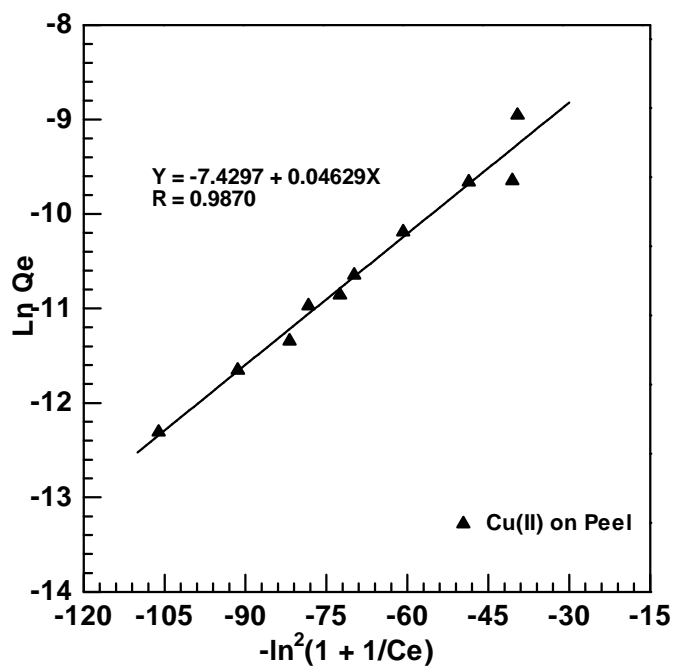
_____

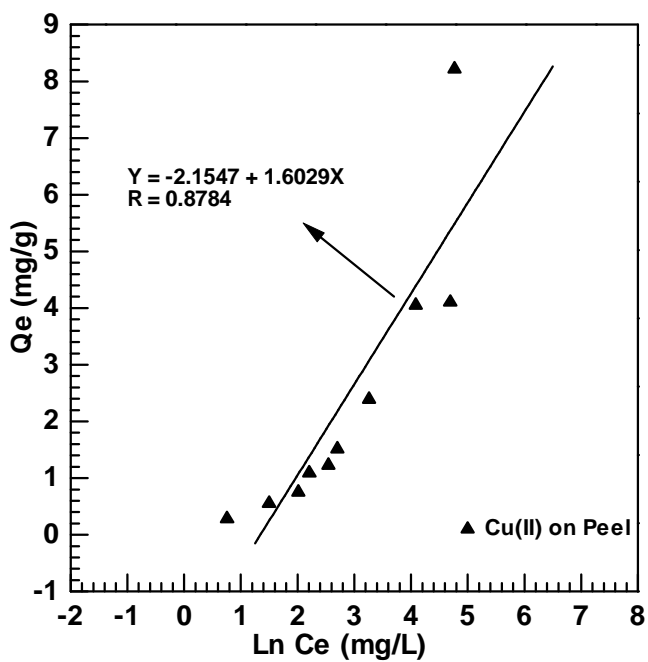**Fig. 13. Linearized Dubinin–Radushkevich equation for Cu(II)**

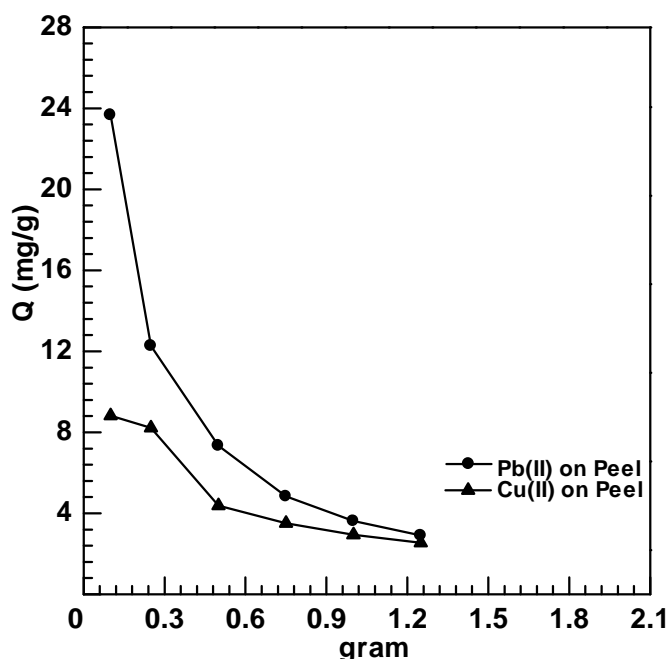**Fig. 14. Linearized Temkin equation for Cu(II)**

859

_____

Figure 15. Effect of Biomass Dosage on Pb(II) and Cu(II) biosorption by *Dimocarpus longan* **peels; 25 mL metal solution, concentration = 150 mg/L for Pb(II) and 200 mg/L for Cu(II); pH of Pb(II) and Cu(II) on peels = 5.0 and 4.0; mass of biosorbent = 0.25 g; contact time = 90 min for both ions; stirring speed = 200 and 100 rpm for Pb(II) and Cu(II) on peels; biosorbent size = 180 μm**

CONCLUSION

The batch studies were performed to determine the optimum sorption conditions of Pb(II) and Cu(II) ions on peels of *Dimocarpus longan* for Pb(II) was pH = 5, contact time = 90 min and stirring speed = 200 rpm. While for Cu(II) was pH = 4, contact time = 90 min and stirring speed = 100 rpm.

The equilibrium data generated by varying the contact time of these ions with peels (under optimum conditions) were found to fit the pseudo first-order, pseudo second-order, Elovich and Intraparticle diffusion equations. Based on the correlation of determination (R), these kinetic models were able to describe the equilibrium data in the order : $2^{nd} > 1^{st} >$ Intraparticle > Elovich. It was predicted that these ions were chemically adsorbed with the rate constant for Pb(II) greater than that for Cu(II). It might be due to the electronegativity and ionic radii of Pb(II) > Cu(II) and they were adsorbed at slightly different sites. Another result was no competitive biosorption to be found in their binary solutions (absorbed at different sites).

Analyzed equilibrium data generated by varying initial concentrations of Cu(II) under optimum conditions were found to fit the Langmuir, Freundlich, D-R and Temkin adsorption isotherms with R of D-R $\approx$ Freundlich > Temkin > Langmuir. Both Freundlich and D-R models predicted that Cu(II) was chemically absorbed on peels. In addition, Temkin result indicated that chemisorption was endothermic. However, Pb(II) on peels could be modeling by linear adsorption isotherm.

REFERENCES

[1] NTA Ghani; GAE Chaghaby. *International Journal of Latest Research in Science and Technology*, **2014**, 3(1), 24-42.
[2] MA Abuh; GK Akpomie; NK Nwagbara; EC Nwabor. *International Journal of Engineering Science Invention*, **2013**, 2(6), 27-35.
[3] RSD Castro; L Caetano; G. Ferreira; PM Padilha; MJ Saeki; LF Zara; MAU Martines; GR Castro. *Ind. Eng. Chem. Res.*, **2011**, 50, 3446-3451.
[4] H Nawaz; Bhatti; Rubina; Khadim; M Asif; Hanif. *Iran. J. Chem. Eng.*, **2011**, 30(4), 81-88.
[5] DA Naidu; P King; KVN Saibaba; VSRK Prasad. *International Journal of Research in Engineering and Technology*, **2013**, 1(2), 35-48.

_____

[6] MI Kurniawan; Z Abdullah; A Rahmadani; R Zein; E Edison. *Asian Journal of Chemistry*, **2014**, 26(12), 3588-3594.

[7] D Singh. *Journal of Environmental Research and Development*, **2007**, 1(3), 227-231.

[8] ME Argun; S Dursun; C Ozdemir; M Karatas. *Journal of Hazardous Materials*, **2007**, 141, 77-85.

[9] WSW Ngah; MAKM Hanafiah. *Journal of Environmental Sciences*, **2008**, 20, 1168-1176.

[10] AM Farhan; AH Al-Dujaili; AM Awwad. *International Journal of Industrial Chemistry*, **2013**, 4(24), 1-8.

[11] OD Uluozlu; A Sari; M Tuzen; M Soylak. *Bioresource Technology*, **2008**, 99, 2972-2980.

[12] XKO Yang; LP Yang; ZS Wen. *Bioresources*, **2014**, 9(2), 2446-2458.

[13] VS Sethu; KS Goey; FR Iffah; CM Khoo; JM Andresen. *Journal of Environmental Research and Development*, **2010**, 5(2), 262-278.

[14] QJM Slaiman; CK Haweel; YR Abdulmajeed. *Iraqi Journal of Chemical and Petroleum Engineering*, **2010**, 11(3), 23-32.

[15] VO Njoku; AA Ayuk; EE Ejike; EE Oguzie; CE Duru; OS Bello. *Australian Journal of Basic and Applied Sciences*, **2011**, 5(8), 101-110.

[16] Y Liu; YJ Liu. *Saparation and Purification Technology*, **2008**, 61, 229-242.

[17] YS Ho; G Mckay. *Water, Air, and Soil Pollution*, **2004**, 158, 77-97.

[18] YS Ho. *Journal of Hazardous Materials*, **2006**, 136, 681-689.

[19] AH Sulaymon; SE Ebrahim; MJM Ridha. *Environ Sci Pollut Res.*, **2012**.

[20] MA Adebayo; AA Adebayo; JF Adediji; OT Adebayo. *The Pacific Journal of Science and Technology*, **2012**, 13(2), 283-293.

[21] DSSR Raju; VN Rao; PR Prasad; NC Babu. *International Journal of Engineering Science and Advanced Technology*, **2012**, 2(6), 1577-1581.

[22] NBA Hadi; NAB Rohaizar; WC Sien. **2011**, 1(5), 49-55.

[23] H Zheng; D Liu; Y Zheng; S Liang; Z Liu. *Journal of Hazardous Materials*, **2009**, 167, 141-147.

[24] CS Gulipalli; B Prasad; KL Wasewar. *Journal of Engineering Science and Technology*, **2011**, 6(5), 586-605.

[25] DLM Stojanovic; A Zarubica; M Purenovic; D Bojic; T Andjelkovic; LJ Aleksandar. *Water SA.*, **2011**, 37(3), 303-312.

[26] AM Awwad; AM Farhan. *American Journal of Chemistry*, **2012**, 2(4), 238-244.

[27] VK Gupta; D Pathania; S Agarwai. *Environ Sci Pollut Res.*, **2012**.

[28] XJ Xiong; XJ Meng; TL Zheng. *Journal of Hazardous Materials*, **2010**, 175, 241-246.

[29] JR Gonzalez; FP Vargas; IC Rodriguez; E Rodriguez; JR Arana; RF Hernandez; JR Flores. *Revista Mexicana De Ingenieria Quimica*, **2007**, 6(3), 295-300.

[30] Y Wu; J Zhou; Y Wen; L Jiang; Y Wu. *Appl Biochem Biotechnol.*, **2012**.

[31] AGD Prasad; MA Abdullah. *Journal of Applied Sciences in Environmental Sanitation*, **2009**, 4(3), 273-282.

[32] SM Hasany; R Ahmad. *Journal of Environmental Protection*, **2006**.

[33] N Tichaona; MN Maria; M Emaculate; C Fidelis; G Upenyu; N Benias. *International Journal of Scientific and Technology Research*, **2013**, 2(4), 199-206.